Chemistry 410B Exam 5 Spring 2009
Solutions

1. **40 points.**

   (a) Draw a line connecting the statement on the left with the most appropriate explanation on the right.

   - $\Delta_{\text{mix}} S > 0$ because $\boxed{\text{D}}$ S increases with V for each substance
   - $\Delta_{\text{vap}} H$ decreases with T because $\boxed{\text{A}}$ C_{Pm} is bigger for the liquid than for the gas
   - vapor pressure increases with T because $\boxed{\text{C}}$ more energy per molecule is available to break intermolecular bonds
   - water has a higher T_f than propane because $\boxed{\text{B}}$ dispersion forces are generally weaker than hydrogen bonds
   - water melts at a constant T as heat is added because $\boxed{\text{E}}$ the average energy per degree of freedom remains constant

   (b) The boiling point for isobutane (2-methylpropane) is 261.3 K. Use Trouton's rule to estimate the standard enthalpy of vaporization. **Solution:** Trouton's rule predicts that $\Delta_{\text{vap}} S_m^{\ominus}$ is roughly $8R$ to $13R$, so $\Delta_{\text{vap}} H_m^{\ominus} = T_b^{\ominus} \Delta_{\text{vap}} S_m^{\ominus}$ should be between $\boxed{17 \text{ and } 28\,\text{kJ mol}^{-1}}$. The actual value is $21.3\,\text{kJ mol}^{-1}$.

   (c) From the phase diagram for isobutane, give T and P for

   i. the critical point: $\boxed{408\,\text{K},\ 36\,\text{bar}}$

   ii. the triple point: $\boxed{114\,\text{K},\ 0.02\,\text{bar}}$

   iii. the standard state melting point: $\boxed{114\,\text{K},\ 1.0\,\text{bar}}$

2. Find an expression for each of the following in terms of $\Delta_{\text{vap}} H_m^{\ominus}$ and $T_b^{\ominus}$ or their derivatives:

   (a) $\Delta_{\text{vap}} E_m^{\ominus}$

$$= \Delta_{\text{vap}} H_m^{\ominus} - \Delta_{\text{vap}}(P^{\ominus} V_m) \approx \Delta_{\text{vap}} H_m^{\ominus} - P^{\ominus} V_m(g) = \boxed{\Delta_{\text{vap}} H_m^{\ominus} - RT_b^{\ominus}}.$$

   (b) $\Delta_{\text{vap}} F_m^{\ominus}$

$$= \Delta_{\text{vap}} E_m^{\ominus} - T_b^{\ominus} \Delta_{\text{vap}} S_m^{\ominus} = (\Delta_{\text{vap}} H_m^{\ominus} - RT_b^{\ominus}) - \Delta_{\text{vap}} H_m^{\ominus} = \boxed{-RT_b^{\ominus}}.$$

   (c) $\Delta_{\text{vap}} \mu^{\ominus}$ at constant S

$$= \Delta_{\text{vap}} \left(\frac{\partial H}{\partial n}\right)_{S,P^{\ominus}} = \boxed{\Delta_{\text{vap}} H_m^{\ominus}} \text{ at constant } S.$$

   (d) $C_{Pm}(g) - C_{Pm}(l)$ at $T_b^{\ominus}$ and 1 bar

$$= \left(\frac{\partial H_m(g)}{\partial T}\right)_{P^{\ominus},n} - \left(\frac{\partial H_m(l)}{\partial T}\right)_{P^{\ominus},n}\Bigg|_{T_b^{\ominus}} = \left(\frac{\partial H_m(g) - H_m(l)}{\partial T}\right)_{P^{\ominus},n}\Bigg|_{T_b^{\ominus}}$$

$$= \left(\frac{\partial \Delta_{\text{vap}} H_m^{\ominus}}{\partial T}\right)_{P^{\ominus},n}\Bigg|_{T_b^{\ominus}}$$

3. It takes a $17.3\,\mathrm{J\,K^{-1}}$ change in entropy to heat 0.300 mol of glycerol from a solid at $T_f^\circ = 291\,\mathrm{K}$ to a liquid at 331 K. The heat capacities are $150\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for the solid and $221.9\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for the liquid. Find $\Delta_{\mathrm{fus}}H_m^\circ$. **Solution:** This is a two-step process, and we can write expressions for the entropy change at each step. The $\Delta_{\mathrm{fus}}H_m^\circ$ is then related to the $\Delta_{\mathrm{fus}}S_m^\circ$ by the temperature T_f°:

$$\begin{aligned}\Delta S &= \Delta S_{\mathrm{vaporization}} + \Delta S_{\mathrm{heating\ liq}}\\ &= n\frac{\Delta_{\mathrm{fus}}H_m^\circ}{T_f^\circ} + nC_{Pm}(l)\ln\frac{T_f^\circ}{T_1}\\ \Delta_{\mathrm{fus}}H_m^\circ &= T_f^\circ\left[\frac{\Delta S}{n} - C_{Pm}(l)\ln\frac{T_f^\circ}{T_1}\right]\\ &= (291\,\mathrm{K})\left[\frac{17.3}{0.300} - (221.9)\ln\frac{331}{291}\right](\mathrm{J\,K^{-1}\,mol^{-1}})\\ &= \boxed{8.46\,\mathrm{kJ\,mol^{-1}}}.\end{aligned}$$

4. $\mathrm{OsO_4}$ sublimes ($\Delta_{\mathrm{sub}}H_m^\circ = 56.9\,\mathrm{kJ\,mol^{-1}}$) with vapor pressure of 0.013 bar at 298 K. Estimate the vapor pressure at 325 K. **Solution:** The Clausius-Clapeyron equation is partly based on the idea that the volume change upon vaporization is essentially equal to the volume of the gas that forms. This assumption applies just as well to sublimation, where we go from the solid to the gas directly. Although we don't have the boiling point, we can integrate the differential form of the Clausius-Clapeyron equation (Eq. 20.36) from any lower limit, in this case P=0.013 bar and $T = 298\,\mathrm{K}$:

$$\begin{aligned}\int_{0.013\,\mathrm{bar}}^{P} d\ln P' &= -\frac{\Delta_{\mathrm{sub}}H_m^\circ}{R}\int_{298\,\mathrm{K}}^{325\,\mathrm{K}} d\left(\frac{1}{T'}\right)\\ \ln\frac{P}{0.013\,\mathrm{bar}} &= \frac{\Delta_{\mathrm{sub}}H_m^\circ}{R}\left(\frac{1}{298\,\mathrm{K}} - \frac{1}{325\,\mathrm{K}}\right) = 1.908\\ P = (0.013\,\mathrm{bar})e^{1.908} &= \boxed{0.088\,\mathrm{bar}}.\end{aligned}$$